Vapor-Liquid Equilibria and Densities of Ternary Mixtures of Fluorinated Ethers with hydrofluorocarbons as R22 Alternatives.

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Abstract

Vapor pressure data below the normal boiling point are presented for ternary mixtures that are prepared from the following chemicals: perfluoro [methylethyl ether] (RE-218), pentafluorodimethylether (RE-125), 1,1,1 trifluorodimethylether (RE-143a), dimethylether (RE-170), 1,1,1,2 tetrafluoroethane (R-134a), 1,1,1 trifluoroethane (R-143a), 1,1 difluoroethane (R-152a), fluoroethane (R-161), and difluoromethane (R-32). Liquid-liquid phase separation in the binary mixtures RE-218/RE-170 and RE-218/R-161 is eliminated with the ternary mixtures, RE-218/RE-143a/RE-170 and RE-218/R-134a/R-161. A sufficient amount of vapor pressure data were obtained for these ternary mixtures to calculate vapor-liquid phase relations using van Laar equations for ternary mixtures. Vapor pressure data are also reported for a number of ternary mixtures containing RE-125. Liquid density data and the critical parameters are reported for the equimolar mixtures, RE-218/R-134a/R-161, RE-125/R-32/R-152a, and RE-125/R-32/R-134a, which are judged to have a high potential as R-22 alternatives based on their boiling point and critical temperature.

Keywords: Vapor-liquid Equilibria, Vapor Pressure, Perfluoro[ethylmethylether], Pentafluorodimethylether, R-22, Refrigerants.

I. Introduction

The search for R-22 replacements has identified binary azeotropic mixtures of perfluoro[ethylmethylether] (RE-218) with partially fluorinated ethane derivatives or the partially fluorinated ether, 1,1,1 trifluoromethylmethylether (RE-143a). These mixtures have boiling points lower than –30°C and critical temperatures higher than 80°C [1-3]. The boiling points and critical temperatures should be compared to those of R-22, -40.1°C and

96°C respectively. However, other binary mixtures investigated, such as RE-218/R-161 or RE-218/RE-170, (R-161 and RE 170 refer to fluoroethane and dimethylether, respectively). that yield low boiling points approaching that of R-22 have high liquid-liquid phase separation temperatures which may be a factor in refrigeration applications.

In order to eliminate the liquid-liquid phase separation temperatures for binary mixtures containing RE-218, 1,1,1,2 tetrafluoroethane (R-134a) or RE-143a are added to the binary mixtures producing the ternary mixtures, RE-218/RE-143a/RE-170 and RE-218/R-134a/R-161 and the vapor pressures of these mixtures at various compositions are studied. In addition ternary mixtures containing pentafluorodimethyl ether (RE-125) are investigated to determine if lower boiling points and higher critical temperatures that approach those of R-22 can be achieved. It is the purpose of this paper to report the results of these investigations.

I. Experimental Methods and Results

For a description of the experimental methods the reader is referred to the authors' previous publications [2-5]. Briefly the vapor pressures below the boiling point were measured to within ±0.5 kPa using MKS capacitance pressure sensors and the temperatures were measured to within ±0.1 K using a copper constantan thermocouple calibrated against a precision Guildline platinum resistance thermometer. The mixtures were prepared to a prescribed mole fraction to with 0.5% accuracy by condensing the components of the mixture into the sample bulb from a calibrated volume. The critical temperature was measured by slowly raising the temperature of the sample in a sealed tube until the disappearance of the meniscus was observed. The saturated liquid density, ρ_l, and diameters, $\overline{\rho}$ [= $(\rho_l + \rho_g)/2$, ρ_g being the saturated vapor density], were measured as function of temperature to with 1kg/m^3 by preparing several samples of differing weight in a precision bore tube (25 cm in length) and measuring the displacement of the meniscus from the bottom of the tube with a Gaertner cathetometer. The chemicals used in this work were synthesized to 99.5% purity, excepting R-161 (CH$_3$CH$_2$F) which was purchased from PCR. The purity of R-161 was verified to be 99.5% by a combination of ^{1}H and ^{19}F NMR spectroscopy, FT-IR spectroscopy, and GC-MS spectroscopy.

The results of the vapor measurements are presented in Tables 1 through 4 and the results of the density measurements are presented in Table 5. The vapor pressures of the ternary mixtures containing RE-218 are presented in Tables 1 and 2 at a number of compositions. One of these ternary mixtures contains RE-218 which has a high fluorine content and RE-170 which contains no fluorine. These two components would form very nonideal binary mixtures whose boiling point in principle could be sufficiently lowered below those of the pure components to approach the boiling point of R-22. However the nonideality of these mixtures is so great that liquid-liquid phase separation would occur up to temperatures above the normal boiling point. The liquid-liquid phase separation is eliminated by adding the third component, RE-143a (CF$_3$OCH$_3$), with an intermediate fluorine content. Effectively the nonideality could be tuned by adjusting the content of RE-143a to produce the optimal boiling point for the resulting ternary mixture. For this reason we have investigated numerous compositions of these mixtures and the measured vapor

Table 1.

Experimental vapor pressure below the normal boiling point as a function of temperature and mole fraction ratio for RE-218/RE-143a/RE-170 Mixtures.

70:15:15		47.1:26.4:26.4		45:35:20		40:20:40		35:35:30		33:33:33	
$T(^oC)$	P (kPa)	T(^oC)	P (kPa)	T (^oC)	P (kPa)	T (^oC)	P (kPa)	T (^oC)	P (kPa)	T (^oC)	P (kPa)
-55.6	31.5	-58.9	26.1	-52.0	36.9	-57.0	31.5	-62.8	20.0	-57.1	28.0
-52.2	38.1	-55.6	31.6	-50.0	41.2	-54.9	35.6	-58.1	26.9	-53.0	35.5
-48.9	45.3	-52.5	38.1	-48.0	46.4	-52.8	40.1	-54.5	33.1	-50.6	40.5
-45.7	53.3	-49.2	45.3	-45.7	52.4	-51.2	43.9	-51.5	39.2	-48.0	46.8
-42.9	61.2	-46.5	52.1	-43.7	57.9	-49.2	48.8	-48.7	45.9	-45.4	53.6
-40.2	69.6	-43.5	60.8	-41.9	63.3	-47.3	53.7	-46.1	52.7	-43.1	60.1
-36.8	80.9	-41.4	67.7	-40.5	68.1	-45.6	58.8	-43.8	59.3	-40.9	67.1
-34.9	88.8	-38.9	76.5	-38.2	76.0	-43.8	64.5	-41.6	66.3	-38.3	76.8
-33.5	94.1	-37.3	82.1	-36.2	83.5	-42.3	69.7	-39.4	73.5	-37.2	80.5
-32.5	98.5	-35.9	87.9	-34.1	92.1	-40.5	76.1	-37.6	80.5	-35.4	87.1
		-34.5	93.6	-32.4	99.3	-38.7	82.8	-35.4	88.5	-34.0	93.3
		-33.5	98.5			-37.0	89.5	-34.4	93.1	-32.7	98.5
						-36.0	93.9	-33.0	98.8		
						-34.9	98.4				

30:30:40		25.5:25.5:49		20:20:60		20:60:20		15:15:70		10:10:80	
T (^oC)	P (kPa)	T(^oC)	P (kPa)	T(^oC)	P (kPa)	T (^oC)	P (kPa)	T (^oC)	P (kPa)	T (^oC)	P (kPa)
-64.6	18.8	-59.8	25.5	-59.8	25.9	-62.8	17.5	-60.0	27.1	-57.4	31.3
-60.2	24.8	-56.0	32.0	-56.2	32.7	-56.9	25.3	-56.4	33.3	-54.5	37.5
-56.2	31.3	-53.1	38.3	-53.4	38.5	-53.3	31.3	-53.4	39.5	-51.5	44.8
-53.3	37.1	-50.6	43.9	-50.7	45.3	-49.7	38.8	-51.2	44.8	-49.2	50.9
-50.4	43.9	-48.0	50.5	-48.5	51.1	-45.9	47.5	-49.0	50.7	-46.5	58.9
-47.6	50.8	-45.5	57.6	-46.3	57.3	-42.6	55.5	-46.8	57.1	-45.6	61.7
-45.1	57.5	-43.1	65.2	-44.0	64.4	-39.2	65.5	-44.6	63.7	-43.9	66.9
-42.5	65.9	-41.0	72.1	-42.1	70.8	-37.2	72.4	-42.5	70.8	-42.4	72.0
-40.0	74.4	-38.7	80.5	-40.4	77.3	-34.8	80.8	-40.7	77.7	-41.0	77.5
-38.4	80.3	-37.0	87.2	-37.2	89.3	-32.6	88.9	-38.9	84.1	-39.5	83.3
-36.7	86.8	-35.4	93.3	-36.4	93.1	-31.6	93.5	-37.1	92.3	-37.8	89.6
-35.0	93.3	-34.3	99.1	-35.0	98.9	-30.5	98.7	-35.6	98.5	-36.5	95.1
-34.0	98.0									-35.6	98.4

Table 2

Experimental Vapor Pressure below the normal boiling point as a function
of temperature and mole fraction ratio for RE-218/RE-143a/RE-170 Mixtures

85:5:10		74:10.5:15.5		60:15:25		50:18.6:31.4		45:45:10		40:40:20		40:22.1:37.9		33.3:33.3:33.3	
T(°C)	P (kPa)	T(°C)	P (kPa)	T (°C)	P (kPa)	T (°C)	P (kPa)	T (°C)	P (kPa)	T (°C)	P (kPa)	T (°C)	P (kPa)	T (°C)	P (kPa)
-47.6	54.9	-47.7	60.5	-54.2	47.3	-55.2	42.8	-48.4	48.8	-54.4	37.6	-52.8	49.2	-55.1	40.0
-45.7	59.1	-46.1	64.3	-52.3	52.1	-53.7	46.7	-46.9	52.9	-52.5	41.7	-51.3	53.6	-52.5	46.0
-44.0	62.7	-45.0	67.9	-50.5	56.8	-52.2	50.8	-45.6	56.8	-50.6	46.3	-50.0	57.3	-50.8	50.5
-42.1	67.2	-43.2	72.9	-48.4	62.8	-50.3	56.3	-44.2	61.2	-48.8	51.1	-49.0	60.5	-49.0	55.6
-40.7	71.3	-42.0	76.8	-47.0	67.2	-48.9	60.5	-42.7	65.7	-46.6	57.2	-47.9	64.4	-47.2	61.3
-39.5	75.1	-40.9	80.7	-45.6	72.0	-47.5	64.9	-41.4	70.3	-45.0	62.4	-46.7	68.1	-45.7	66.1
-38.2	79.1	-39.6	84.7	-43.7	78.0	-46.0	69.7	-39.9	75.6	-43.1	68.7	-45.6	72.0	-44.1	71.5
-37.0	83.2	-38.3	89.5	-42.3	83.3	-44.5	75.2	-38.6	80.1	-40.9	76.4	-44.2	76.8	-42.2	78.4
-35.8	87.1	-37.0	94.8	-40.9	88.4	-43.2	79.9	-37.3	85.6	-38.3	86.4	-43.2	80.7	-40.8	83.6
-34.7	91.6	-36.0	98.7	-39.7	93.2	-42.0	85.2	-36.0	90.9	-36.7	93.1	-42.2	84.5	-38.7	92.3
-33.5	95.7			-38.2	99.2	-40.8	89.9	-35.2	94.7	-35.3	99.7	-41.0	89.9	-37.3	98.7
-32.8	98.3					-39.6	94.1	-34.2	98.8			-39.9	94.0		
						-38.7	98.5					-38.8	98.5		

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Table 2 (continued)

30:30:40		30:26:44		25:30:45		20.7:56:23.3		15:20:65		10:10:80		10:80:10	
$T(^{o}C)$	P (kPa)	T(^{o}C)	P (kPa)	T (^{o}C)	P (kPa)	T (^{o}C)	P (kPa)	T (^{o}C)	P (kPa)	T (^{o}C)	P (kPa)	T (^{o}C)	P (kPa)
-54.0	44.8	-57.7	37.7	-53.7	45.3	-49.5	45.9	-54.8	47.6	-58.0	43.3	-48.6	42.0
-52.5	48.9	-55.4	42.9	-52.4	48.9	-48.0	50.5	-53.4	51.2	-56.0	48.5	-47.0	45.6
-51.0	53.1	-53.8	46.9	-50.7	53.7	-46.0	55.9	-51.8	56.3	-54.1	54.1	-45.3	49.6
-49.5	57.3	-51.3	54.0	-48.9	59.1	-44.3	61.2	-50.1	61.5	-52.3	58.9	-43.8	53.9
-48.1	61.9	-50.1	57.7	-47.4	63.9	-42.9	66.1	-48.6	66.7	-50.7	64.5	-42.3	58.1
-46.6	66.8	-48.8	61.5	-45.7	69.7	-41.3	71.5	-46.9	72.1	-48.8	70.1	-39.9	65.3
-45.2	71.7	-47.8	64.8	-43.4	78.3	-39.8	76.9	-45.5	77.5	-47.4	75.7	-38.4	69.9
-43.5	77.7	-46.7	68.7	-41.9	83.2	-38.3	82.3	-44.1	83.3	-45.8	81.6	-37.1	74.8
-42.0	83.5	-45.4	73.3	-40.8	88.3	-36.7	88.8	-42.6	88.8	-44.4	87.3	-35.6	79.9
-40.8	88.5	-43.9	78.4	-39.6	93.5	-35.5	93.9	-41.4	94.1	-42.9	93.3	-34.4	85.3
-39.6	93.3	-42.6	83.7	-38.4	98.1	-34.5	98.5	-40.3	98.5	-41.5	99.1	-32.9	90.9
-38.4	98.8	-41.4	88.9									-31.0	99.5
		-40.1	93.7										
		-38.9	99.3										

Table 3

Experimental vapor pressures below the boiling point for equimolar ternary mixtures containing RE-125

RE-125/R-143a/R-161		RE-125/R-143a/R-152a		RE-125/R-143a/R-134a		RE-125/R-32/R-161		RE-125/R-32/R-152a		RE-125/R-32/R-134a		RE-125/RE-143a/R-143a		RE-125/RE-143a/R-161	
$T(^oC)$	P (kPa)	T(^oC)	P (kPa)	T (^oC)	P (kPa)	T (^oC)	P (kPa)	T (^oC)	P (kPa)	T (^oC)	P (kPa)	$T(^oC)$	P (kPa)	T (^oC)	P (kPa)
-61.2	34.3	-52.1	48.4	-59.7	31.9	-62.4	37.6	-58.5	40.4	-58.1	41.3	-52.4	46.1	-54.3	32.3
-59.0	38.4	-50.3	53.2	-57.1	36.7	-60.2	42.9	-56.6	44.9	-56.3	45.6	-50.7	50.3	-51.3	38.4
-56.9	43.2	-48.3	58.9	-54.6	41.9	-58.4	47.3	-54.7	49.9	-54.3	51.1	-49.1	54.1	-48.6	44.5
-54.8	48.1	-45.9	66.3	-52.9	46.4	-56.7	52.1	-53.1	54.4	-52.5	56.0	-47.3	59.5	-45.7	51.5
-52.9	53.2	-44.7	70.4	-50.9	51.6	-54.9	56.8	-51.6	58.7	-50.9	60.8	-45.5	64.8	-43.0	59.1
-50.9	59.1	-43.5	74.4	-48.8	57.9	-53.3	62.3	-50.0	63.6	-49.2	66.7	-43.9	70.1	-40.8	65.9
-49.1	64.8	-42.3	78.5	-46.0	66.0	-52.1	66.1	-48.3	69.7	-46.6	76.1	-42.5	74.9	-38.3	73.9
-47.3	70.5	-40.9	84.0	-44.3	71.9	-50.5	71.7	-46.9	74.9	-45.3	80.7	-41.0	80.4	-35.2	86.0
-45.5	77.5	-39.7	88.1	-42.6	78.4	-47.8	81.6	-45.3	80.4	-43.8	86.8	-39.4	86.4	-32.4	97.9
-44.0	83.1	-38.3	94.4	-41.1	83.9	-45.8	90.1	-43.9	86.3	-42.3	92.8	-38.2	90.9		
-42.8	88.3	-37.2	98.9	-39.5	90.5	-44.7	95.2	-42.3	92.0	-40.6	100.3	-37.4	94.5		
-41.4	93.5			-37.5	99.1	-43.5	100.3	-40.8	99.5			-36.4	98.8		
-40.2	98.9														

Table 4

Experimental vapor pressure measurements as a function of temperature for selected ternary mixtures between the normal boiling point and critical temperature.

RE218/R134a/R161		RE125/R32/R134a		RE125/R32/R152a	
$T(^oC)$	P (kPa)	T(^oC)	P (kPa)	T (^oC)	P (kPa)
14.2	698.3	14.6	811.5	11.6	736
20.7	839.6	17.2	875.2	16.8	859
25.0	944.9	20.2	951.9	22.0	996
30.1	1082.6	24.9	1080.9	27.2	1148
35.1	1235.1	30.2	1243.7	32.4	1317
40.2	1402.7	35.2	1409.7	37.6	1503
45.5	1596.9	40.0	1585.5	42.8	1709
50.5	1797.7	46.3	1832.0	48.0	1935
56.3	2046.5	50.2	2000.5	53.2	2182
60.5	2249.4	55.2	2230.9	58.3	2453
65.4	2499.7	60.1	2471.5	63.5	2748
70.1	2763.2	66.1	2789.6	68.7	3071
74.3	3015.5	71.1	3074.7	73.9	3423
77.4	3214.0	74.0	3245.3	79.1	3807
		80.8	3675.8	84.3	4226
				89.5	4682

Table 5

Measured saturated liquid densities and diameters between the boiling point and critical temperature for selected ternary mixtures.

RE218/R134a/R161			RE125/R32/R134a			RE125/R32/R152a		
T(^oC)	P(kPa)	T(^oC)	T(^oC)	P(kPa)	T(^oC)	T(^oC)	P(kPa)	T(^oC)
24.1	1133.1	593.1	22.4	1176.2	611.1	22.7	1150.3	591.1
31.0	1102.3	583.5	27.7	1150.2	603.4	30.6	1125.2	580.1
35.5	1080.4	577.3	36.1	1111.5	591.1	35.8	1104.9	572.8
40.7	1053.4	570.1	41.2	1087.4	583.6	41.9	1075.8	564.2
45.6	1038.3	563.3	46.6	1060.5	575.8	50.8	1034.0	551.8
51.6	1002.0	555.0	51.3	1035.9	568.9	56.8	993.1	543.4
55.5	978.5	549.6	58.8	999.5	557.9	61.1	968.8	537.4
60.4	947.8	542.8						

pressures are given in Table 1. Likewise the vapor pressures of RE-218/R-134a/R-161 are examined at a number of compositions and are presented in Table 2.

Unlike mixtures containing RE-218, the vapor pressure of mixtures containing RE-125 exhibit nearly ideal behavior [3]. Therefore detailed composition studies of these mixtures were not performed. Rather a number of ternary mixtures were examined which contained RE-125 and various other components in equimolar amounts. The vapor pressure measurements from these studies are presented in Table 3.

From these investigations it was judged based on boiling point and critical temperature that three of the equimolar mixtures; RE-218/R-134a/R-161, RE-125/R-134a/R-161 and   RE-125/R-32/R-152; have high potential as R-22 alternatives. Vapor pressure measurements for these mixtures were extended to temperatures above the boiling point, approaching the gas-liquid critical temperature and are presented in Table 4. The saturated liquid density and diameters measured for these mixtures are presented in Table 5.

III. Discussion and Conclusions

In order to analyze the vapor-liquid phase diagram for the ternary mixtures containing RE-218 and identify possible azeotropic compositions, a 3-component van Laar analysis described by Wohl [6] was applied to the vapor pressure data in Tables 1 and 2. It begins by fitting the vapor pressure data to the following van Laar equations by the least squares method,

$$P = P_1^o x_1 \gamma_1 + P_2^o x_2 \gamma_2 + P_3^o x_3 \gamma_3 \tag{1}$$

where γ_1, γ_2 and γ_3 are the activity coefficients of components 1, 2 and 3, respectively; P_1^o, P_2^o and P_3^o are the vapor pressures for pure components 1-3 and X_1, X_2 and X_3 are the liquid mole fractions of the components, respectively. The vapor phase mole fractions, y_1 and y_2 are estimated from

$$y_1 = \frac{x_1 P_1^o \gamma_1}{P_t}, \tag{2}$$

$$y_2 = \frac{x_2 P_2^o \gamma_2}{P_t}, \tag{3}$$

The activity coefficients for ternary liquid mixtures are given by,

$$\log \gamma_1 = \frac{\left[x_2^2 A_{1-2} \left(\frac{A_{2-1}}{A_{1-2}} \right)^2 + x_3^2 A_{1-3} \left(\frac{A_{3-1}}{A_{1-3}} \right)^2 + x_2 x_3 \frac{A_{2-1}}{A_{1-2}} \frac{A_{3-1}}{A_{1-3}} \left(A_{1-2} + A_{1-3} - A_{3-2} \frac{A_{1-3}}{A_{3-1}} \right) \right]}{\left(x_1 + x_2 \frac{A_{2-1}}{A_{1-2}} + x_3 \frac{A_{3-1}}{A_{1-3}} \right)^2}, \tag{4}$$

$$\log \gamma_2 = \frac{\left[x_3^2 A_{2-3} \left(\frac{A_{3-2}}{A_{2-3}} \right)^2 + x_1^2 A_{2-1} \left(\frac{A_{1-2}}{A_{2-1}} \right)^2 + x_3 x_1 \frac{A_{3-2}}{A_{2-3}} \frac{A_{1-2}}{A_{2-1}} \left(A_{2-3} + A_{2-1} - A_{1-3} \frac{A_{2-1}}{A_{1-2}} \right) \right]}{\left(x_2 + x_3 \frac{A_{3-2}}{A_{2-3}} + x_1 \frac{A_{1-2}}{A_{2-1}} \right)^2}, \tag{5}$$

$$\log \gamma_3 = \frac{\left[x_1^2 A_{3-1}\left(\frac{A_{1-3}}{A_{3-1}}\right)^2 + x_2^2 A_{3-2}\left(\frac{A_{2-3}}{A_{3-2}}\right)^2 + x_1 x_2 \frac{A_{1-3}}{A_{3-1}}\frac{A_{2-3}}{A_{3-2}}\left(A_{3-1} + A_{3-2} - A_{2-1}\frac{A_{3-2}}{A_{2-3}}\right)\right]}{\left(x_3 + x_1 \frac{A_{1-3}}{A_{3-1}} + x_2 \frac{A_{2-3}}{A_{3-2}}\right)^2}, \quad (6)$$

where $A_{1\text{-}2}$, $A_{2\text{-}1}$, $A_{1\text{-}3}$, $A_{3\text{-}1}$, $A_{2\text{-}3}$ and $A_{3\text{-}2}$ represent the van Laar parameters as proposed by Wohl [6]. Equations (1) through (6) assume that the vapor fugacity is equal to the partial vapor pressure of the corresponding components.

The temperature dependence of the van Laar coefficients are assumed to be linear with the reciprocal Kelvin temperature. The results of fitting the vapor pressure data in Tables 1 and 2 to these van Laar equations by least squares calculation is given in Table 6. The pure component vapor pressure data needed for these calculations is taken from our previous publications [1,3,7], i.e. vapor pressure data for RE-218, RE-143a, R-161 were obtained from Kul et al. [1], for R-134a from Kul et al. [3], and for RE-170 from Kul [7].

Table 6

Results of the van Laar analysis of the vapor pressure data below the boiling point.

A_{12}	A_{21}	A_{13}	A_{31}	A_{23}	A_{32}
$CF_3OCF_2CF_3(1)/CF_3OCH_3(2)/CH_3OCH_3(3)$ Mixtures (RMS Dev. = 2%)					
$-0.2307 + \dfrac{249.2}{T}$	$5.9947 - \dfrac{1080.4}{T}$	$-4.3277 + \dfrac{1751.9}{T}$	$5.474 - \dfrac{813.4}{T}$	$2.8439 - \dfrac{663.3}{T}$	$0.2278 - \dfrac{53.17}{T}$
$CF_3OCF_2CF_3(1)/CF_3CH_2F(2)/CH_3CH_2F(3)$ Mixtures (RMS Dev.= 1%)					
$-2.9947 + \dfrac{1076.5}{T}$	$2.6721 - \dfrac{329.74}{T}$	$1.3458 + \dfrac{282.53}{T}$	$-6.506 + \dfrac{1825.5}{T}$	$14.225 - \dfrac{3407.5}{T}$	$10.231 - \dfrac{2485.6}{T}$

Using the van Laar Equations and the temperature dependence of the van Laar coefficients, ternary compositions with the same boiling point were calculated and these compositions for various boiling points are presented in ternary composition diagrams, Figures 1 and 2. One can view the lines of constant boiling point on these 2-D diagrams as points on a sheet or surface of a three dimensional ternary diagram in which the normal boiling point would be third dimension. The minima or troughs or valleys on this sheet are identified by directed lines in Figures 1 and 2. For the RE-218/RE-143a/RE-170 mixtures (Figure 1) the trough begins with the azeotropic minimum boiling (-30°C) composition of binary mixture, RE-218/RE-143a, and extends toward increasing mole fractions of the third component, RE-170. The boiling points along the trough decrease to -34 °C. The calculated
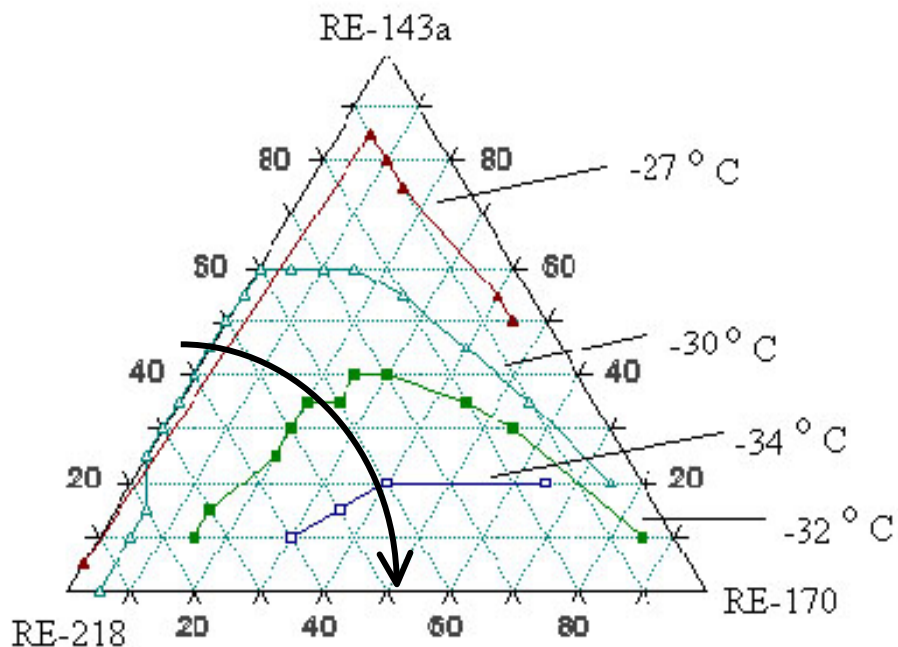
Figure 1.   Boiling point diagram of the RE-218/RE-143a/RE-170 Ternary Mixtures Versus Liquid Mole Fractions of Components.
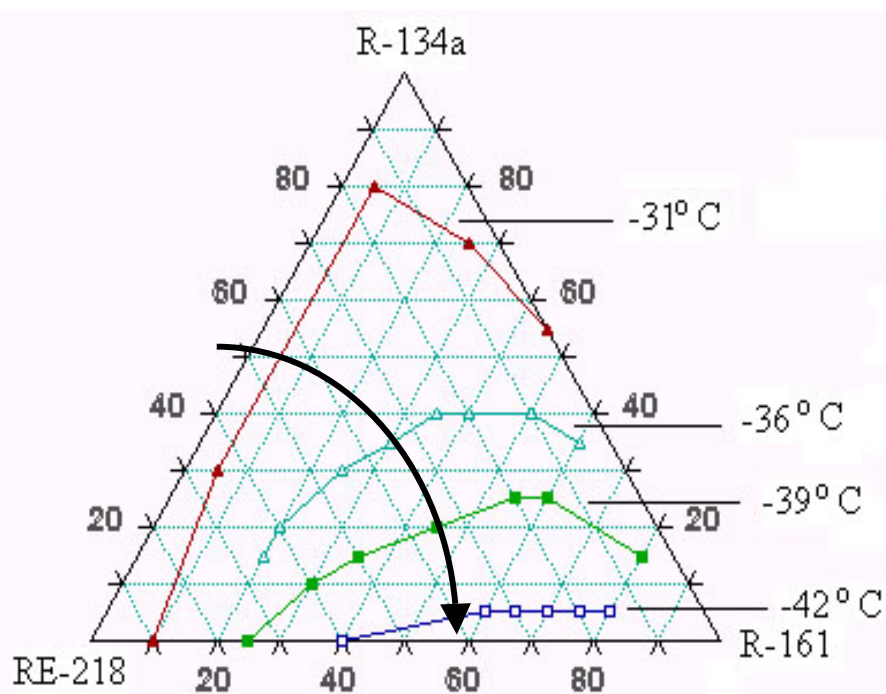

Figure 2.   Boiling Point Diagram of the RE-218/ R-134a/R-161 Ternary Mixtures Versus Liquid Mole Fractions of Components.

liquid and vapor phase compositions at one point along the trough are nearly equal, i.e. the liquid phase mole fractions are; X_1=0.472, X_2=0.264 and X_3=0.264 with a boiling point of –32.8^{o}C and the corresponding vapor phase compositions are y_1=0.508, y_2=0.237 and y_3=0.255, where RE-218, RE-143a and RE-170 are components 1, 2 and 3, respectively. Although this composition is not a true ternary azeotropic composition, it does have azeotropic like behavior and hence the terminology of 'near azeotropic' composition is used.

Figure 2 illustrates that the boiling point behavior of the mixture, RE-218/R-134a/R-161, parallels that of RE-218/RE-143a/RE-170. An azeotropic line or 'trough' begins with the azeotropic composition, 0.48 mole fraction of RE-218, of the binary mixture, RE-218/R-134a, whose azeotropic boiling point is –32°C. The azeotropic line extends toward increasing concentrations of the third component, R-161. As one increases the concentration of CH_3CH_2F, the boiling point rapidly decreases to –42°C at which point liquid-liquid phase separation occurs. The composition along the azeotropic line which is judged the best composition for R-22 refrigerant applications is at equimolar concentrations of the three components. This composition has a boiling point, -36.7^{o}C that is well below that of the binary mixture, RE-218/R-134a. It is also expected to be nonflammable by the rule that the total number of C-F bonds in the mixture exceeds the sum of the total number of C-C and C-H bonds [8]. Mixtures with lower boiling points are expected to be flammable and to have high liquid-liquid phase separation temperatures.

Table 7

Parameters of Equation (7) Obtained by a Least Squares Calculation on
Vapor Pressures Measured Below the Boiling Point for equimolar ternary mixtures.

Mixture	Empirical Parameters (Eq. (7))			Boiling P. (^{o}C)	% RMS Dev
	a	b	c		
RE-125/RE-143a/R-161[a]	47.4876	-4.9541	-3789.5	-31.6	0.3
RE-125/R-134a/R-161[a]	77.9263	-9.6493	-4916.6	-31.8	0.3
RE-218/RE-143a/RE-170	67.5142	-8.0479	-4520.2	-32.1	0.3
RE-125/RE-143a/R-143a	19.0488	-0.6094	-2633.8	-35.8	0.2
RE-125/R-143a/R-152a	88.7409	-11.4379	-5109.6	-36.6	0.2
RE-218/R-134a/R-161	82.5243	-10.4078	-4970.6	-36.7	0.2
RE-125/R-143a/R-134a	47.4327	-4.9688	-3698.5	-37.0	0.4
RE-125/R-143a/R-161	13.0778	0.3573	-2429.4	-39.7	0.3
RE-125/R-32/R-152a	89.0983	-11.4834	-5097.1	-40.3	0.3
RE-125/R-32/R-134a	91.9289	-11.9164	-5206.0	-40.4	0.2
RE-125/R-32/R-161	67.3819	-8.1109	-4289.6	-43.3	0.3
[a]Data taken from Kul et al. [2]					

The vapor phase composition at the equimolar liquid composition indicates fractionation of the low boiling, R-161 component. Consequently, the "near azeotropic" behavior of these mixtures is poorer than RE-218/RE-143a/RE170 mixtures. However, because of their lower boiling point and higher critical temperature, the RE-218/R-134a/R-161 mixture is expected to have a higher potential as an R-22 alternative. The boiling point of the various ternary mixtures containing RE-125 was obtained by fitting the vapor pressure data in Table 3 to the following empirical relation,

$$\ln P = a + b \ln T + \frac{c}{T} \quad , \tag{7}$$

The results are summarized in Table 7 along with related results from prior work [2]. For comparison purposes we have also included in Table 7, results for ternary mixtures containing RE-218 that were investigated in this work. The results are ordered with decreasing boiling point.

IV. Summary of Conclusions

The ternary mixture van Laar analysis [6] are useful for identifying azeotropic and near azeotropic compositions for the nonideal mixtures. A near azeotropic composition is determined for the ternary mixture, RE-218/RE-143a/RE-170 with a mole fraction ratio of 0.472:0.264;0.264 and a boiling point of -32.8°C. However based on the boiling point, the optimal mixture for R-22 replacement that contains RE-218 is the equimolar mixture of RE-218/R-134a/R-161 (See Table 7) with a boiling point of -36.7°C. The optimal mixtures that contain RE-125 are the equimolar mixtures RE-125/R-32/R-134a and RE-125/R-32/R-152a with boiling points of -40.4 and -40.3, respectively (See Table 7). Saturated liquid densities

Table 8

Empirical representations for liquid density, boiling point and critical constants for ternary mixtures with high potential for R-22 replacement.

Mixture	Liquid Density (kg/m^3) (t=Centigrade Temperature)	$t_b(^{\circ}$C)	$t_c(^{\circ}$C)	ρ_c (kg/m^3)	P_c (kPa)
RE-218/R-134a/R-161	1210.7 - 2.5911*t - 0.02869*t^2	-36.7	87.6	504	3930
RE-125/RE-32/R-134a	1276.0 - 4.3302*t - 0.00642*t^2	-40.4	86.2	515	4038
RE-125/R-32/R-152a	1189.4 - 0.59099*t - 0.04965*t^2	-40.3	89.5	498	4682

and diameters were measured for these mixtures. Also the vapor pressures were measured up to temperatures approaching the critical temperature (See Table 4).

A parametric representation of the liquid density data along with the critical constants are presented in Table 8. The critical density in Table 8 was obtained by extrapolating the diameters to the critical temperature and the critical pressure is calculated from the empirical relation ($\ln P = \alpha + \beta/T_r + \gamma \ln T_r + \delta T_r^6$, where $T_r = T/T_c$) that has been fitted to vapor

pressure data (see Table 4) for temperatures ranging from the boiling point up to near the critical temperature.

These data along with vapor pressure data, Benson et al. database for ideal gas heat capacities [9], and modified corresponding states methods [4] can be used to estimate the Coefficient of Performance of these mixtures as refrigerants using methods described in Bare [10] and Morrison and McLinden [11]. Such estimates are beyond the scope of this present paper will be reported in future publications.

Acknowledgements

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